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Formation of Aromatic *O*-Silylcarbamates from Aminosilanes and Their Subsequent Thermal Decomposition with Formation of Isocyanates

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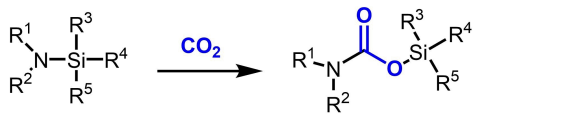
A novel phosgene-free route to different isocyanates starts from CO_2 and aminosilanes (cf. silylamines) to form so-called carbamoyloxysilanes (*O*-silylcarbamates), i.e., compounds with the general motif $R^1R^2N–CO–O–SiR^3R^4R^5$ as potential precursors. We focused on the insertion reaction of CO_2 into Si–N bonds of substrates with cyclic (mostly aromatic) amine substituents, i.e., $PhNHSiMe_3$, $(PhNH)_2SiMe_2$, $PhCH_2NHSiMe_3$, p-(MeO)$C_6H_4NHSiMe_3$, o-$C_6H_4(NHSiMe_3)_2$, 1,2-$C_6H_{10}(NHSiMe_3)_2$, o-$C_6H_4(NHSiMe_3)(CH_2NHSiMe_3)$ and 1,8-$C_{10}H_6(NHSiMe_3)_2$. Compared to previously investigated aminosilanes these reactions are hindered due to the reduced nucleophilicity/basicity of the N-atoms. Whereas slightly increased CO_2 pressure (8 bar) and prolonged reaction times (24 h) were sufficient to overcome hindrance of the insertion into, e. g., $PhNHSiMe_3$, intermolecular effects in some two-fold $NHSiMe_3$ functionalized substrates led to partial mono-insertion (e. g., into o-$C_6H_4(NHSiMe_3)(CH_2NHSiMe_3)$) or intra-molecular condensation of the intermediate insertion product in case of 1,8-$C_{10}H_6(NHSiMe_3)_2$ to form 1H-perimidin-2(3H)-one and other side products. Thermal treatment of mono-silylated O-silylcarbamates $RHN–CO–O–SiR'_3$ resulted mainly in the formation of substituted ureas $(RHN)_2CO$, whereas desired isocyanates could not be detected in these cases. Therefore, we continued our studies focussing on *N,O*-bissilylated precursors, which were obtained by an additional *N*-silylation of the *O*-silylated carbamates. This allowed the successful formation of isocyanates. As a sole byproduct hexamethyldisiloxane is formed. In all cases, known as well as yet unknown substances were characterised by ^1H, ^{13}C and ^{29}Si NMR spectroscopy, along with X-ray diffraction analysis for crystallized solids.

Introduction

In the context of the more and more evolving topic of carbon dioxide utilization for the production of various crucial chemicals, we aim at employing CO_2 as an oxygen source as well as a carbon source in the synthesis of compounds such as (poly) siloxanes, urea derivatives and isocyanates.[1–4,5,6,7] One key step is the insertion reaction of CO_2 into *Si*–NR^1R^2 bonds of aminosilanes with formation of the desired $R^1R^2NC(O)OSi$ motif (cf. carbamoyloxysilane, carbamatosilane, *O*-silylcarbamate; *Si* = tetravalent silicon with three further substituents), as shown in Scheme 1. These compounds may serve as precursors for isocyanates, formation of which depends on cleavage of the *O*-silylcarbamate motif with release of a suitable leaving group R^1OSi. In this context, we refer to "aminosilanes" in a narrow sense as those compounds containing Si-bound amine groups, i.e., Si–N bonds (cf. silylamines).



R^{1-2} = H, alkyl, aryl, allyl
R^{3-5} = alkyl, aryl, allyl, NR^1R^2

R^{1-2} = H, alkyl, aryl, allyl
R^{3-5} = alkyl, aryl, allyl, $OCONR^1R^2$

Scheme 1. Generic reaction pathway of carbon dioxide insertion into aminosilanes.

Mechanistic considerations of the insertion of CO_2 into Si–N bonds have been published earlier.[1,6] In brief, at first a nucleophilic approach of the N atom toward the CO_2 carbon atom occurs. Two alternative proceeding routes arise depending on the nitrogen-bonded substituents. (i) The CO_2 oxygen atom approaches the Si atom, thus forming a four-membered cyclic transition state, which was postulated by *Kraushaar et al.*,[1] and represents a plausible pathway for any kind of aminosilane ($R^{1,2}$ may be combinations of H, alkyl, aryl, allyl). (ii) Alternatively, amine-bound hydrogen might attract and be transferred to a CO_2 oxygen atom and lead to the formation of a carbamic acid. In the latter case, the final silylcarbamate motif is accomplished by migration of both the COOH proton and the still N-bound silyl group. Strong bases might support the

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second pathway by deprotonation of the acid and thereby stabilizing the intermediate form.

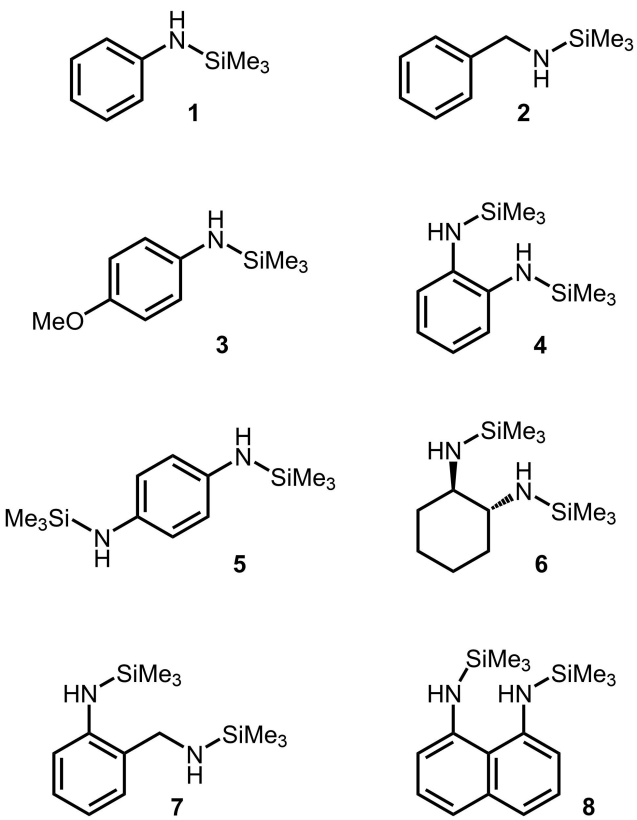
In our previous studies of *O*-silylcarbamate syntheses, the CO_2 insertion reaction included bubbling of CO_2 into a solution of the aminosilane in THF at ambient pressure and low temperature.[4] For aliphatic aminosilanes the corresponding *O*-silylcarbamates formed in high yields within 20 minutes or less. The same procedure works equally fine for di-, tri- and tetra-aminosilanes with sterically less demanding substituents. With aromatic aminosilanes, however, similar reactions at ambient conditions failed.[1–3,7,8]

Being the simplest representative of the class of aromatic aminosilanes, a lot of experiments have been done using *N*-trimethylsilylaniline (**1**), though a successful insertion reaction by the mentioned procedure could not be achieved.[7] The formation of [*O*-(trimethylsilyl)carbamato]benzene (**1a**) has been studied by different groups previous to the present work, though.[9] In doing so, *Zoeckler and Laine* found a way to synthesize **1a** starting from **1** and carbon dioxide including transition metal catalysis and temperatures of 100 °C and above in a Parr bomb reactor.[9] Another synthesis pathway was investigated by *Kozyukov et al.* By heating aniline and different *O*- and *N*-silylcarbamates for several hours the desired product could be obtained in yields of up to 40 %.[10] *Knausz et al.*[11] and the research group of *Belova*[12] were able to synthesize compound **1a** in yields of up to 45 % by mixing aniline with CO_2/hexamethyldisilazane, a so called *N*-siloxycarbonylating reagent, either for a longer period or by heating to 60 °C for a few hours. Similar systems include CO_2/hydridosilane and CO_2/*N,N'*-bis(trimethylsilyl)carbodiimide.[13] Working with hexamethyldisilazane as well, *Sheludyakov et al.* were able to produce **1a** by mixing the silazane with aniline hydrochloride and carbon dioxide.[14] *Yamamoto et al.* found a way to access **1a** by refluxing either *tert*-butyl- or isopropyl-trimethylsilyl-carbonate along with aniline in diethyl ether for one hour.[15] The formation of **1a** in a procedure of heating a mixture of *N*-phenyl-*O*-alkyl-carbamates and trimethylsilyl iodide up to 50 °C has been described by *Jung and Lyster*, affording the desired product in 60 % yield.[16] Quite recently, *Fuchter et al.*[17] published a way of synthesizing *O*-silylcarbamates by heating *N*-silylamines in supercritical carbon dioxide as an intermediate step to produce various ureas. In addition to aliphatic silylamines, the aniline and *p*-anisidine derivatives have been part of their investigations.

While a wide range of trimethylsilylated amine compounds are known in the literature, the number of aromatic *O*-silylated carbamates is limited. Quite some research has been done by *Xu et al.*[18] On the way of preparing various ureas from CO_2 and silylamines, they proposed the formation of silylcarbamates as intermediate products. Their reaction procedure includes exposition of the aminosilane to 1–5 atm CO_2 in a J-Young NMR tube and refluxing the mixture at 75–150 °C for several hours to collect the desired urea afterwards. The described silylcarbamate, a derivative of *p*-anisidine, was only detected in NMR spectra and could not be isolated, though. *Knausz et al.*[19] studied the formation of various trimethylsilylated *N*-aryl-substituted carbamates (i.e., methyl-, chloro-, bromo- and methoxy-substituted aniline derivatives) by the reaction of aniline derivatives with hexamethyldisilazane and CO_2 at increased temperatures and using $CoCl_2$ as a catalyst. *Knausz et al.*[20] also investigated *N,O*-bis(trimethylsilyl)-carbamates and carbonyl compounds on the way to the formation of imines and *O*-methyl-oximes. These results along with related research on *O*-trimethylsilyl-*N,N*-dialkylcarbamates were summarized in a review.[21]

The CO_2 insertion reaction into diaminosilanes of the type $(RR'N)_2SiMe_2$ has been thoroughly investigated in our group in the past.[1–3,22] The reports include a method to produce oligo- and polysiloxanes along with *N*-substituted urea derivatives starting from diaminosilanes $(RR'N)_2SiMe_2$ in a reaction with CO_2 to yield insertion products $(RR'N{-}CO{-}O)_2SiMe_2$ and subsequent thermal decomposition affording the desired compounds.[4] All previous works focused on aliphatic side chains R and R' bonded to the nitrogen atoms. In the present study, we extended our investigations of CO_2 insertion into Si–N bonds onto the predominantly aromatic compounds shown in Scheme 2.

As those compounds possess a high potential as precursors due to the existing structure motif of isocyanates, we also extended our research toward the synthesis of isocyanates. First results are discussed subsequent to the carbon dioxide insertion.



Scheme 2. Overview of aminosilanes investigated within this paper for the insertion of carbon dioxide into Si–N bonds.

Results and Discussion

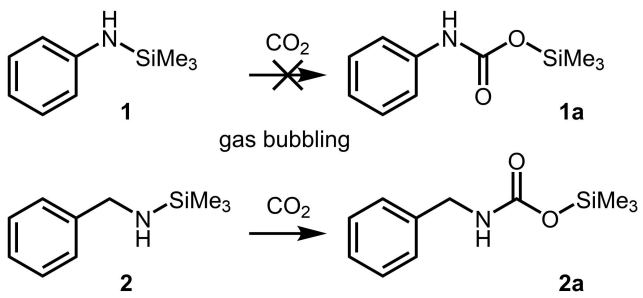
Carbon dioxide insertion into aromatic aminosilanes

Initial attempts at CO_2 insertion into *N*-trimethylsilylaniline (**1**) by gas bubbling under ambient conditions – analogous to the very successful reactions of aminosilanes with aliphatic substituents on the N-atoms – failed, even upon increased reaction time. Addition of the strong base 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), which increases the total amount of dissolved carbon dioxide in the solvent due to the formation of a CO_2-complex[23], afforded traces of the corresponding silylcarbamate **1a**. After an hour of gas bubbling at ice cooling, the aminosilane still represents the main compound in the product mixture, though.

A CH_2-linkage between the aromatic ring and the nitrogen atom changes the behaviour completely, affording the silylcarbamate **2a** easily by bubbling CO_2 into *N*-trimethylsilylbenzylamine (**2**) in THF (Scheme 3).[7]

Exposure of a THF solution of **1** to CO_2 at 8 bar in an autoclave (for picture see Supporting Information, Figure S1) for 24 hours at room temperature finally afforded pure **1a** in good yield, even without the use of a catalyst. The product, a white solid, was recovered from the solution upon removal of the solvent under reduced pressure. Subsequent recrystallization from *n*-pentane finally afforded colorless needles of **1a** in yields of up to 80 %. Spectroscopic analysis of the crystals confirmed the identity and purity of the insertion product, and a single-crystal X-ray diffraction analysis confirmed a structure which had previously been reported by *Sheludyakov et al.*[14] As our structure determination delivered a model of somewhat better bond precision, our data is included in the Supporting Information (Figure S8). In the autoclave experiments, we observed that addition of DBU supported both the insertion reaction and crystallization as visible by spontaneous formation of colorless needles immediately after opening the autoclave container and transferring the pale-yellow liquid into a Schlenk flask. Nonetheless, elevated CO_2 pressure and prolonged reaction times are still essential, as reducing the time to 2 hours or the pressure to 2 bar lowered the product yield significantly.

While the first experiments were performed in the small autoclave with an overall reaction volume of 5 mL, we proceeded toward a reaction scale of up to 50 mL, increasing the amount of aminosilane used from approximately 1 g to almost 10 g. Under the given parameters of 24 hours at room temperature and a CO_2 pressure of 8 bar, the insertion reaction proceeds as smooth as on a small scale.



Scheme 3. CO_2 insertion into the Si–N bonds of compounds **1** and **2** following the common procedure of gas bubbling through a solution of the aminosilane in THF.[2]

In order to gain insights into the reasons for the different behaviour of aliphatic and aromatic aminosilanes at the exposure to carbon dioxide and the need for a raised pressure, calorimetric measurements of the CO_2 insertion reaction were performed. Calorimetric analyses using aminosilane **1** revealed an enthalpy of −76 kJ/mol for the insertion reaction at a pressure of 4 bar CO_2. Hence, the reaction is thermodynamically favoured, but kinetically slightly hampered in this case. Steric aspects might influence the insertion reaction of CO_2 into the Si–N bond of **1**. Additionally, the lone pair of the nitrogen atom is delocalized across the aromatic π-electron system, which decreases the nucleophilicity of the amine and hampers the insertion reaction on a kinetic level. This is most likely the main reason for the observed differences between the two described experimental methods.

A similar insertion reaction can be observed using dianilinodimethylsilane $(PhNH)_2SiMe_2$, which afforded the two-fold insertion product di(*N*-phenylcarbamoyloxy)dimethylsilane by the common procedure (8 bar, 24 h) as a main product (for experimental data see Supporting Information). The formation of colorless needle-shaped crystals, which were suitable for X-ray diffraction analysis, revealed the crystal structure of that yet unknown compound (see Figure S57 in Supporting Information). Side products included the proposed formation of a mono-insertion product, where only one of two Si–N bonds included carbon dioxide.

In the following, we studied the insertion reaction of CO_2 into some derivatives of **1**. Starting from *p*-anisidine, which carries a methoxy group in para-position, we synthesized *N*-trimethylsilyl-*p*-anisidine (**3**) as a brownish liquid in a first step, followed by the successful insertion reaction using the above-mentioned autoclave method to obtain 4-[*O*-(trimethylsilyl) carbamato]methoxybenzene (**3a**), which crystallized from the mother liquor as colorless needles after partial removal of the solvent. Single-crystal X-ray structure determination confirmed the identity of the product and matches the results reported by *Belova et al.*[24] The CO_2 insertion proceeds almost quantitatively, leaving only small traces of the aminosilane in the reaction solution. Complete removal of the solvent led to a brownish solid, which was obtained in a yield of 91 %.

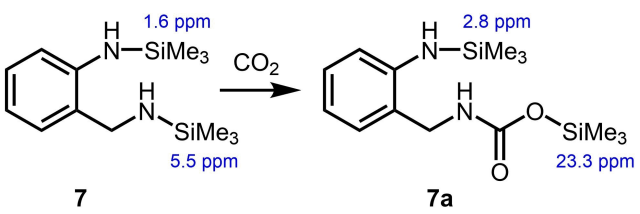
1,2-Bis(trimethylsilylamino)benzene (**4**), which bears another trimethylsilylated amine function in ortho-position, also undergoes CO_2 insertion along the autoclave procedure with formation of compound **4a**. In this case, insertion of CO_2 into both Si–N bonds was observed in a basically quantitative manner. Neither traces of the aminosilane **4** nor those of the product of single CO_2 insertion were detected. Under the same conditions, a reaction starting from *p*-phenylendiamine via 1,4-bis(trimethylsilylamino)benzene (**5**) proceeds in the same way to yield the corresponding dicarbamate species, which has been obtained using a different method by *Mironov et al.*[25]

In addition to aromatic aminosilanes, which reveal some kinetic hindrance of CO2 insertion, (+/−)- *trans*-1,2-bis (trimethylsilylamino)cyclohexane (**6**) is an alicyclic representative, which exhibits hindered CO_2 insertion along the gas bubbling protocol (affording a product mixture consisting of larger amounts of the unconsumed aminosilane in addition to the desired carbamato compound). For this case, the autoclave procedure (8 bar, 24 h) proved useful once again, delivering the desired product of two-fold CO_2-insertion in almost quantitative yield. In addition to insufficient reaction time, steric aspects of the two trimethylsilyl groups might influence the insertion of CO_2 into the Si–N bonds. With alkyl substituents of related steric demand (e. g. cyclohexyl), simple aminosilanes were reported to undergo CO_2 insertion quantitatively under mild conditions. The gas bubbling procedure afforded the desired insertion product, *O*-(trimethylsilyl)carbamatocyclohexane, in an isolated yield of 95% and gave crystals suitable for single-crystal X-ray diffraction analysis, which revealed the crystal structure of this so far unknown compound (see Supporting Information, Figure S64).

An interesting observation was made with a combination of aliphatic and aromatic amine environments, i.e., in *N,N'*-bis (trimethylsilyl)-2-aminobenzylamine (**7**). NMR spectroscopic data acquired from the crude reaction mixture after the general autoclave procedure suggest selective mono-insertion of CO_2 into the aliphatic silylamine group with formation of compound **7a** (Scheme 4).

In **7a**, the ^{29}Si NMR shift value of 2.8 ppm indicates a nitrogen-bound $SiMe_3$ group rather than a silyl carbamate. The latter tend to produce peaks in the range of 20–25 ppm as confirmed by many of our own results (e. g., δ^{29}Si(**1a**) = 22.2 ppm). In addition to the signals of the main product **7a** another peak (at 23.8 ppm) with noticeably lower intensity was observed in the ^{29}Si NMR spectrum. We suspect that the second insertion reaction of CO_2 into the aromatic aminosilane group with formation of the dicarbamate species does occur to some extent, but is kinetically much more hampered.

The identity of the main product **7a** was confirmed by crystallographic structure determination (Figure 1). After applying a CO_2 pressure of 8 bar to the aminosilane for a period of 23 hours and removing the solvent afterwards, a yellow, highly viscous liquid was received. Upon storage in the refrigerator, needle shaped crystals formed, which were suitable for X-ray crystallographic measurements. The crystal structure revealed intramolecular hydrogen bonds between O2 and H1n with a



Scheme 4. Proposed CO_2 insertion into one Si–N bond of compound **7** with formation of **7a** based on the results of NMR spectroscopic measurements. Associated ^{29}Si NMR shifts are listed in blue.

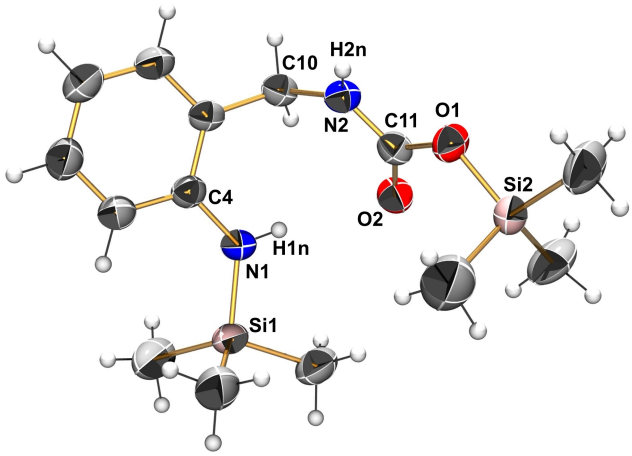
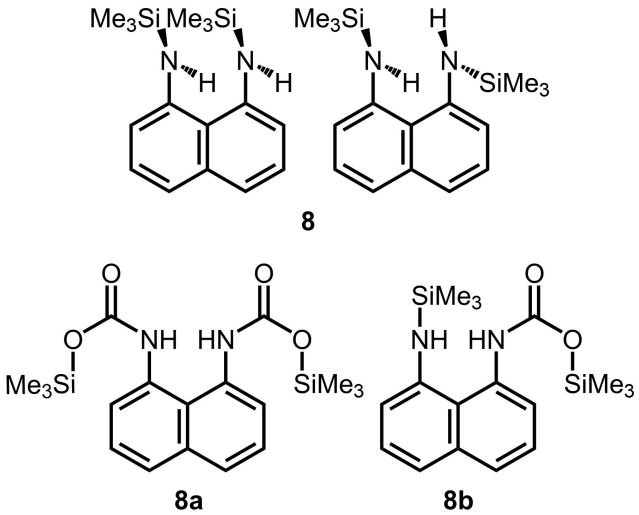


Figure 1. Molecular structure of **7a** in the crystal (displacement ellipsoids are drawn at the 50% probability level, selected atoms are labelled, the lower occupancy part of the disordered $SiMe_3$ group at Si2 is omitted for clarity). Only one of the three crystallographically independent (but conformationally similar) molecules in the asymmetric unit is shown. Selected bond lengths [Å] and angles [°]: Si1–N1 1.725(2), Si2–O1 1.681(2), C11–O1 1.344(3), C11–O2 1.229(3), C11–N2 1.325(3), Si1–N1–C4 131.0(2), Si2–O1–C11 125.4(2).

separation O1···N1 of 3.000(3) Å (as well as between the corresponding O and H atoms of the other two molecules in the asymmetric unit with O···N separations of 3.012(3) and 3.061(3) Å). We assume it is due to these hydrogen bonds, and the hindered rotation of the aryl-NH–$SiMe_3$ moiety resulting therefrom, that even at CO_2 pressure of 8 bar formation of the dicarbamate is hindered.

Extension of the aromatic system to a naphthalene core decreased the ability to include carbon dioxide at the given parameters. The use of 1,8-bis(trimethylsilylamino)naphthalene (**8**) did not lead to the desired CO_2 insertion product at all. The steric effects of the two $NHSiMe_3$ groups in peri-position presumably pose a greater steric hindrance. Even prolonged reaction time (up to 72 h) and a pressure of 8 bar CO_2 only resulted in a partial conversion of the aminosilane (see Scheme 5).

The aminosilane **8** apparently forms two rotation isomers due to the orientation of the two $NHSiMe_3$ groups. Hence, the ^{29}Si-inept NMR spectrum of **8** shows two peaks, at 1.4 and 3.4 ppm. After application of 8 bar CO_2 for 72 h a bunch of signals is found in the ^{29}Si-inept NMR spectrum of the crude product mixture (for spectra see Supporting Information, Figure S48). The peaks of the starting material **8** (1.2 ppm, 3.3 ppm) remain the peaks with the highest intensity in the same intensity pattern, indicating an equilibrium state in solution. A group of four signals is found in the area of 23 ppm, with a peak at 22.8 ppm showing the second highest intensity of the full spectrum. We associate those signals with oxygen-bound $SiMe_3$ groups of the di- and mono-insertion product **8a** and **8b**, each compound appearing in two rotation isomers themselves. The signals for the corresponding nitrogen-bound $SiMe_3$ group of the mono-insertion product appear at 13.0 and 13.8 ppm: As expected, two signals for the rotation isomers. In



Scheme 5. Rotation isomers of **8** and proposed insertion products **8a** and **8b**.

addition, the appearance of hexamethyldisiloxane (7.2 ppm) can be detected. The latter would be the side product during condensation of a product of single CO_2 insertion with formation of a urea, which formed clusters of beige crystalline plates (which appeared red because of the adherent mother liquor) after several days and was identified as 1H-perimidin-2(3H)-one by X-ray crystal structure determination (Figure 2).

Preparation of isocyanates

The investigated class of compounds might be suitable as precursors for crucial chemicals such as urea derivatives, siloxanes and isocyanates. Especially the latter became the current focus of our research. The approach of obtaining isocyanates by thermal cracking of silyl carbamates has been reported in the literature. *Greber and Kricheldorf*[26] found a way of reducing the decomposition temperature of carbamates by silylation of carbamic acid chlorides and urethanes producing mono-silylated *N*-silylcarbamates. Finally, thermal cracking of the *N*-silylcarbamates yielded the corresponding isocyanates. *Mironov*[27] summarized routes starting from silylamines and related silicon compounds to obtain isocyanates, such as direct phosgenation of *N*-silylamines, thermolysis of mono-silylated *N*-silylurethanes and thermolysis of silylhydroxamic acids. *Mironov* also reported the formation of isocyanates in high yields upon heating mono-silylated *O*-silylcarbamates or carbamates along with $PhSiCl_3$. As trimethylsilanol is liberated during decomposition of the *O*-silylcarbamate, large amounts of the isocyanate undergo hydrolysis yielding the symmetric dialkylurea. Similar reactions have been mentioned by *Lebedev et al.* to transfer this synthesis onto isocyanates with other aliphatic and allylic side chains.[28] In contrast, *Oertel et al.*[29] and *Breederveld et al.*[30] described the *O*-silylcarbamates as mostly stable to thermal treatment, reporting distillation rather than decomposition upon heating.

In previous studies, we already investigated the thermal decomposition of *O*-silylcarbamates, thereby setting the focus on aliphatic diaminosilanes as mentioned in the introduction. A postulated mechanism for thermal decomposition of such compounds includes the intermediate formation of isocyanates, which react quickly with free amine to yield the observed urea derivatives.[2,22] The isolation of isocyanates remained problematic, though, as the side reaction with the amine (affording the corresponding urea derivative) was always favoured. A similar decomposition pathway has been postulated by *Knausz et al.*[31] in 1983 for aliphatic and allylic trimethyl-substituted *O*-silylcarbamates refuting the thesis of *Mironov et al.*, which has been mentioned above. By autosilylation the corresponding *N,O*-bissilylated carbamate species is formed in the condensed phase along with an equivalent of both carbon dioxide and amine (see Scheme 6). At temperatures around 100–120 °C the intermediate bissilylated species decomposes with formation of the desired isocyanate and release of hexamethyldisiloxane,

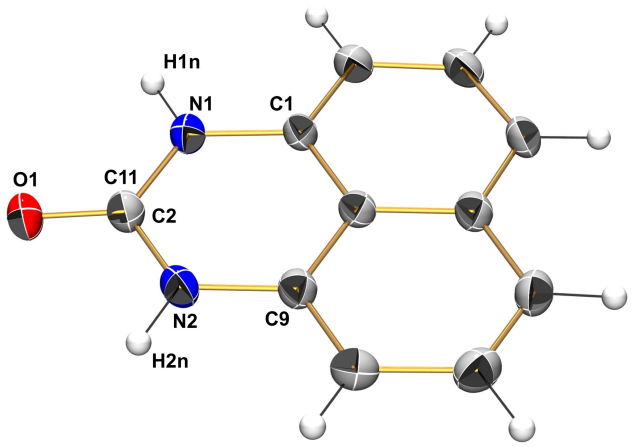
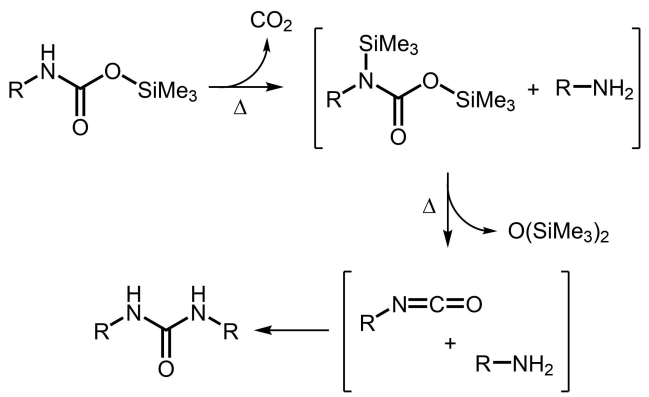


Figure 2. Molecular structure of the cyclic urea derivative 1H-perimidin-2(3H)-one formed by the insertion reaction of CO_2 into **8** (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: O1–C11 1.245(2), N1–C1 1.403(2), N1–C11 1.359(2), N2–C9 1.404(2), N2–C11 1.360(2), O1–C11–N1 121.72(13), O1–C11–N2 121.53(13), N1–C11–N2 116.74(12).



Scheme 6. Postulated pathway for the formation of urea derivatives by thermal treatment of *O*-silylcarbamates.[31]

though a quick reaction with the amine occurs, eventually forming the corresponding 1,3-dialkylurea. This postulated pathway has been adopted by *Fuchter et al.* in the synthesis of *O*-silylcarbamates and ureas in supercritical CO_2.[17] Neither of them reports the analytical proof not to mention the isolation of the isocyanates, though.

Taking the above mentioned information into account, we extended our own research onto aromatic *O*-silylcarbamates. As the insertion reaction of carbon dioxide afforded the corresponding *O*-silylcarbamate in high yields, thermolysis experiments followed. So far, we have been investigating the thermal decomposition of **1 a** in a distillation apparatus for micro quantities with cold finger (short-path distillation) by heating the white solid in a vacuum. Already 10 minutes after starting the experiment the deposition of a white solid in upper parts of the still was visible. After brief interruption of the experiment (for taking a sample of the white solid for NMR spectroscopic analysis) heating was resumed, which finally led to the condensation of a clear colorless liquid at the cold finger and more solid in higher parts of the still. NMR studies revealed the presence of **1 a** in every sample reaching from the bottom vessel of the still through to the safety flask after the still, which was cooled by liquid nitrogen. In the latter, the accumulation of the more volatile hexamethyldisiloxane (HMDSO) along with aniline was detected. Both compounds next to unconsumed **1 a** were found on the cold finger as well. The white solid turned out to contain traces of 1,3-diphenyl urea in addition to the *O*-silylcarbamate. Comparison with commercially available phenyl isocyanate confirmed the absence of noticeable amounts of that compound in any sample after thermal treatment (cf. grey boxes in Figure 3). These results agree with the postulated mechanism for the thermal decomposition of *O*-silylcarbamates by *Knausz et al.*[31]

To inhibit the side reaction of the isocyanate group with any amine formed, we replaced the nitrogen-bound hydrogen atom in another silylation procedure, which afforded a *N,O*-bissilylated carbamate. Only partial conversion was achieved using trimethylchlorosilane, though better results were obtained by using trimethylsilyl triflate. The silylating agent is added dropwise to a mixture of the *O*-silylcarbamate and Et_3N in *n*-pentane while stirring and cooling in an ice bath. The formation of a slushy precipitate at the bottom of the flask was observed, which is easily removed from the mixture by freezing and decanting the liquid supernatant. Removal of solvent (from the supernatant) under reduced pressure yielded the desired derivative **1 b** as a white solid, which was recrystallized from THF to afford crystals suitable for X-ray crystal structure determination (Figure 4). This method revealed the structure of the so-far unknown molecule *N,O*-bis(trimethylsilyl) carbamatobenzene (**1 b**). It represents a rather novel compound as no aromatic *N,O*-bissilylated carbamates are described in the literature to the current date, while the unsubstituted 'parent' *N,O*-bissilylated carbamate $Me_3SiHN{-}CO{-}O{-}SiMe_3$ may be used

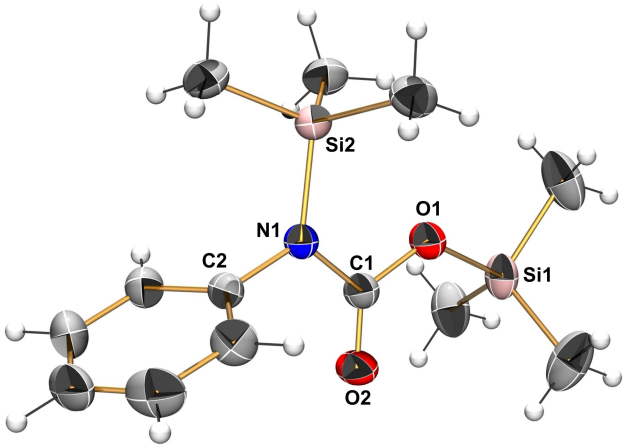


Figure 4. Molecular structure of **1 b** in the crystal (displacement ellipsoids drawn at the 50% probability level). Selected bond lengths [Å] and angles [°]: C2–N1 1.4421(18), N1–Si2 1.7936(13), N1–C1 1.3654(19), C1–O1 1.3555(17), C1–O2 1.2083(19), O1–Si1 1.6890(11), N1–C1–O1 110.99(13), Si2—N1–C1 122.30(10), C1–O1–Si1 123.62(10).

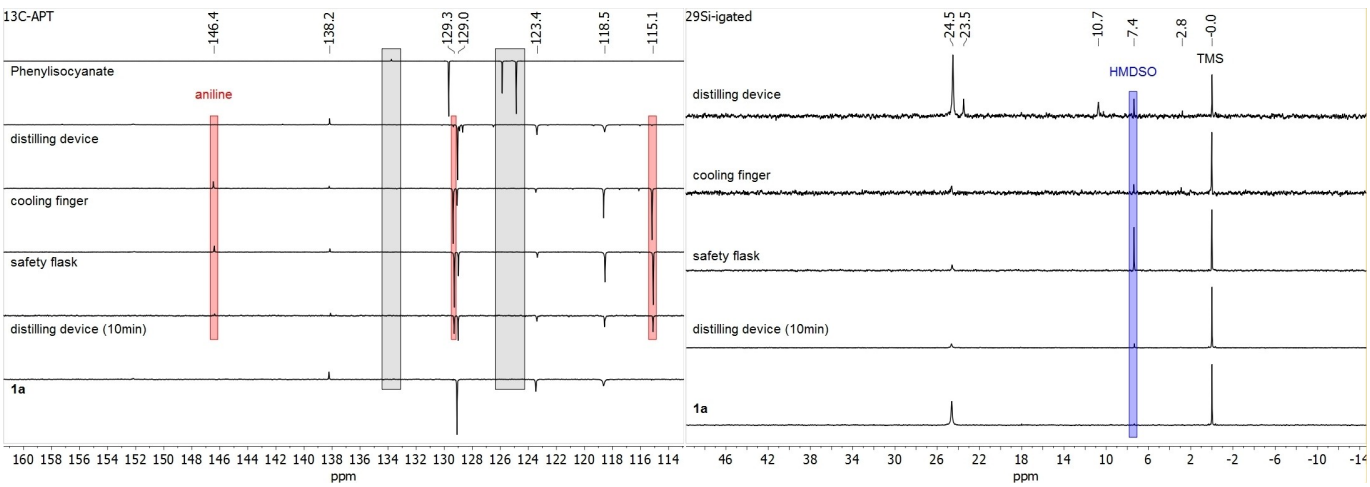


Figure 3. ^{13}C-APT and ^{29}Si NMR spectra of various samples after thermal treatment of **1 a**. For better visualisation only part of the ^{13}C NMR spectra are shown.

as a silylating reagent itself, forming only CO_2 and NH_3 as side products.[32]

By replacing the N-bound hydrogen atom by a trimethylsilyl group the thermal decomposition toward the isocyanate and HMDSO should be favoured. Our experiments of the thermal treatment of **1b** revealed the Kugelrohr (ball tube) distilling apparatus to be a more suitable device for the decomposition reaction. We performed the thermal treatment of **1b** in a three-parted Kugelrohr still yielding the residue, the intermediate fraction inside the oven as well and the outer fraction outside the heating chamber (and cooled by water). While the residue and the intermediate fraction contained a mixture of various aromatic species, which could not be identified clearly, the third fraction in the outer bulb consisted exclusively of the desired phenyl isocyanate and the side product HMDSO, as detected by NMR spectroscopy. After an overall decomposition time of 3 hours no traces of the starting *N,O*-bissilylcarbamate were found in any fraction. Comparison with commercially available phenyl isocyanate clearly proved the presence of that compound in the outer fraction. Additionally, this result was confirmed by ATR-IR spectroscopy (Figure 5), where the corresponding isocyanate band was clearly visible at 2258 cm^{-1} (cf. Ph-NCO: 2247 cm^{-1}).

In the following, we extended our research towards the synthesis of different isocyanates, e. g. benzyl isocyanate, by the described route. The silylation of benzyl amine to gain the *N*-benzyl substituted aminosilane **2**, followed by insertion of CO_2 to yield **2a** and silylation of the nitrogen atom with formation of ω-[*N,O*-bis(trimethylsilyl)carbamato]toluene (**2b**) proceeded in high yields and afforded the desired compounds in high purity as confirmed by NMR spectroscopy.

Thermal treatment of **2b** using a Kugelrohr created the desired benzyl isocyanate in the outer fraction. Whereas the residue and the intermediate fraction contain various silicon-containing species according to the ^{29}Si-inept NMR spectra, HMDSO can be observed as the sole silicon-containing compound in the outer fraction. Those results are confirmed by ^{13}C NMR spectroscopy, where several peaks are visible in the spectra of the residue and the intermediate fraction. The peak of HMDSO at 1.7 ppm arises with the highest intensity in the ^{13}C NMR spectra of the outer fraction. Additionally, the presence of benzyl isocyanate was confirmed (46.4, 126.6, 127.8, 128.7, 137.0 ppm). The peak location and intensity pattern agrees well with the spectrum of a commercially available sample of benzyl isocyanate. Next to that, in very low intensity a peak at 21.2 ppm along with a few peaks in the shift range of phenyl C atoms can be observed. Performing that procedure afforded 1.82 g colorless liquid in the outer bulb starting from 3.13 g of **2b**. Thermolysis of a larger sample of **2b** (8.38 g) with a raised heating rate (direct heating to 300 °C without steps at 200 °C and 250 °C) gave 1.74 g colorless liquid in the outer bulb with a significant increase of the intensity of peaks mentioned last (21.5, 125.5, 128.4, 129.2, 137.9 ppm). In addition, the corresponding signals of benzyl isocyanate vanish completely. Interestingly, the peaks with increased intensity can be assigned to toluene (cf. 21.3, 125.6, 128.5, 129.3, 137.7 ppm[33]). Next to that, another peak with significant intensity was observed at 0.9 ppm, which we assigned to trimethylsilyl isocyanate. The corresponding signal for the isocyanate group can be found at 124.0 ppm as a broad peak of very low intensity. In the associated ^{29}Si-inept NMR spectrum the peak for trimethylsilyl isocyanate was found at 4.2 ppm. Our own measurements of a commercially available sample of trimethylsilyl isocyanate along with an HMBC NMR analysis of the outer fraction confirmed the assignments (see Scheme 7). We suspect the toluene formation being enabled by carbonization of the residue, which turns dark brown during thermal treatment, or by traces of impurities in the starting material such as triethylamine for example.

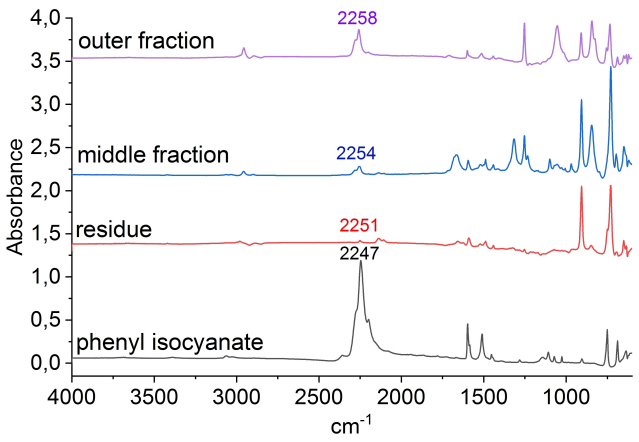
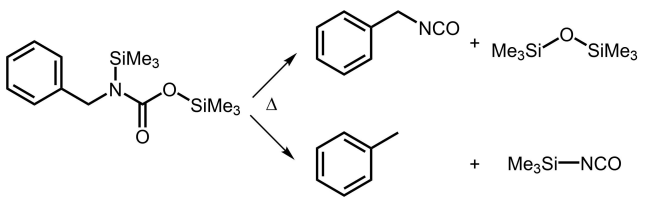


Figure 5. ATR-IR spectra of decomposition fractions in comparison to commercially available phenyl isocyanate.

Conclusions

In our present study we investigated the insertion of CO_2 into silicon nitrogen bonds of aromatic aminosilanes with formation of –N–CO–O–Si– units and successfully establishing an autoclave method to provide the desired products in good yields. Instead of gas bubbling of CO_2 through a THF solution of aminosilane, the starting material has to be exposed to the gas at a pressure of up to 8 bar. Reactions in a scale of up to 10 g aminosilane were performed successfully. Compounds with limited steric hindrance, i.e. those containing only a single N–$SiMe_3$ group as found in $PhNHSiMe_3$ and p-(MeO)$C_6H_4NHSiMe_3$, easily include carbon dioxide at the given parameters. With the newly established method the insertion reaction even proceeded effectively with compounds posing more demanding steric requirements, whereas gas bubbling



Scheme 7. Observed products upon thermal treatment of **2b**.

led to a product mixture. Only the extension of the aromatic system toward a naphthalene derivative still causes problems, as we were not able to clearly identify the desired carbamato-compound so far, and intermediates may already decompose with formation of side products, among them the cyclic urea derivative 1H-perimidin-2(3H)-one.

Embarking in the topic of replacing phosgene in the industrial process of synthesizing isocyanates we managed to successfully decompose aliphatic and aromatic *N,O*-bissilylated carbamate species to gain the desired isocyanate along with hexamethyldisiloxane as a side product. Herein, we show the general proof-of-principle to form isocyanates from aminosilanes and CO_2 without using phosgene. The mentioned procedure still holds potential for optimization, e. g. in-situ silylation to mask the nitrogen bonded proton or variation of thermolysis parameter. Combination of the aminosilane synthesis and CO_2 insertion might be interesting as well. Further investigations on that part include an upscaling to produce the pure isocyanate as well as variation of the carbamate species to increase the variety of products accessible along this route. Especially phosgene-sensitive, low-scale isocyanates produced by smaller companies come into focus of our future research to avoid high costs for safety equipment necessary for the use of phosgene. In addition to that, the introduced synthesis pathway can be adapted to produce industrially relevant diisocyanates. While the production of common diisocyanate compounds such as TDI and MDI is well established, we aim for the synthesis of special chemicals with a small-scale need.

Experimental Section

The syntheses of aminosilanes as well as the insertion reactions were carried out in a dry argon atmosphere using standard Schlenk techniques. The chemicals were purchased from commercial suppliers and purified by distillation. Solvents were dried using a solvent purification system by MBRAUN (for THF) or by storage over molecular sieves for deuterated solvents and *n*-pentane. Solids were dried in a dynamic vacuum at room temperature for at least one hour. Insertion reactions of carbon dioxide were either performed in a smaller, self-made autoclave with a reaction volume of up to 5 mL or in a miniclave of Büchi AG manufactured by C3 Prozess- und Analysentechnik GmbH. The latter could hold up to 200 mL reaction volume in a PTFE inlet or up to 50 mL in an Erlenmeyer flask. While the small autoclave did not offer the possibility to work under fully inert conditions, the miniclave could be loaded and unloaded in an argon atmosphere. Both autoclave systems were charged with CO_2 from Linde with a purity of 5.3.

Solids and liquids have been analysed by nuclear magnetic resonance spectroscopy. ^{1}H, ^{13}C and ^{29}Si NMR spectra of liquid samples were recorded on BRUKER Avance III 500 MHz or BRUKER Nanobay 400 MHz spectrometers. Tetramethylsilane was used as internal standard [$\delta(^{1}H,^{13}C,^{29}Si) = 0$ ppm]. Additional pictures of NMR spectra are included in the Supporting Information. Crystals obtained have been examined by single-crystal X-ray diffraction analysis, either for determination of the unit cell (for compounds of known structure) or for full structure refinement. Single-crystal X-ray diffraction data were collected on a STOE IPDS-2/-2T diffractometer (equipped with a low-temperature device) with Mo–Kα radiation ($\lambda = 0.71073$ Å) using ω scans. Preliminary structure models were derived by solution with ShelXS or ShelXT[34] and the structures were refined by full-matrix least-squares cycles based on F^2 for all reflections using ShelXL[35]. The positions of N-bound hydrogen atoms have been refined without constraints. All other hydrogen atoms were included in the refinement in idealized positions (riding model).

Elemental analysis was performed on a Vario MICRO cube in CHNS mode. Sample preparation occurred under inert conditions inside an argon-flooded glovebox.

Synthesis of Aminosilanes 1 to-8

Compounds **1**–**3** were produced by dropwise addition of trimethylchlorosilane to a solution of the associated amine in the solvent with intense stirring and cooling in an ice bath. (The solution contained triethylamine as a sacrificial base for formation of triethylamine hydrochloride as a white precipitate.) Upon addition of the silane, the reaction mixture was allowed to attain room temperature and was continuously stirred overnight. Afterwards, the precipitate was filtered off, and removal of the solvent from the filtrate (condensation into a cold trap under reduced pressure) afforded the aminosilane as a liquid residue. All relevant data are summarized in Table 1 and Table 2.

For the preparation of aminosilanes **4**–**8**, the starting materials were refluxed for 30 minutes after dropwise addition of trimethylchlorosilane to a mixture of the corresponding amine and triethylamine in the listed solvent. Afterwards, the described procedure of compound **1** was applied.

Table 1. Synthesis and analysis data of aminosilanes **1** to **3**.

	N-trimethylsilylaniline (**1**)	*N*-trimethylsilylbenzylamine (**2**)	*N*-trimethylsilyl-*p*-anisidine (**3**)
amine	4.28 g (46.00 mmol)	5.03 g (46.94 mmol)	5.61 g (45.52 mmol)
Me_3SiCl	5.12 g (47.16 mmol)	5.17 g (47.59 mmol)	5.12 g (47.16 mmol)
Et_3N	5.11 g (50.50 mmol)	4.91 g (48.52 mmol)	4.89 g (48.32 mmol)
solvent	100 ml *n*-pentane	160 ml Et_2O	100 ml *n*-pentane
product	white solid	colorless liquid	orange liquid
yield	7.13 g	7.45 g	7.64 g
	(43.13 mmol, 94 %)	(41.54 mmol, 89 %)	(39.11 mmol, 86 %)
NMR solv.	$CDCl_3$	$CDCl_3$	C_6D_6
^{1}H NMR	6.66–6.59 (m, 5 H, ArH), 3.29 (s, 1	7.16 (m, 2 H, ArH), 7.05 (m, 2 H, ArH), 3.76 (d, 2 H,	6.70 (m, 2 H, ArH), 6.36 (m, 2 H, ArH), 3.45 (s, 3 H,
(400 MHz)	H, HN), 0.21 (s, 9 H, $SiMe_3$)	$^{3}J = 8.0$ Hz, CH_2), 0.55 (s, 1 H, HN), 0.00 (s, 9 H, $SiMe_3$)	OMe), 3.07 (s, 1 H, HN), 0.15 (s, 9 H, $SiMe_3$)
^{13}C NMR	147.4 (ArC), 129.2 (ArCH), 117.5	144.2 (ArC), 128.1 (ArCH), 126.8 (ArCH), 126.3 (ArCH),	152.5 (ArC), 141.1 (ArC), 117.4 (ArCH), 116.2,
	(ArCH), 116.1 (ArCH), 0.0 ($SiMe_3$)	45.9 (CH_2), 0.0 ($SiMe_3$)	115.0 (ArCH), 55.1 (OMe), 0.0 ($SiMe_3$)
^{29}Si NMR	2.7	3.9	1.8

Table 2. Synthesis and analysis data of aminosilanes **4** to **8**.

	1,2-bis (trimethylsilylamino) benzene (**4**)	1,4-bis (trimethylsilylamino) benzene (**5**)	(+/−)-trans-1,2- bis (trimethylsilylamino) cyclohexane (**6**)	*N,N'*-bis(trimethylsilyl)-2-amino-benzylamine (**7**)	1,8-bis (trimethylsilylamino) naphthalene (**8**)
amine	5.01 g (46 mmol)	5.00 g (46.25 mmol)	9.51 g (83 mmol)	5.00 g (41 mmol)	7.30 g (46 mmol)
Me_3SiCl	10.00 g (92 mmol)	10.03 g (92.30 mmol)	18.10 g (167 mmol)	9.00 g (83 mmol)	10.50 g (97 mmol)
Et_3N	9.42 g (93 mmol)	9.38 g (92.68 mmol)	16.95 g (167 mmol)	8.40 g (83 mmol)	9.33 g (92 mmol)
solvent	100 ml THF	140 ml THF	100 ml THF	100 ml THF	100 ml THF
product	orange liquid	yellow solid	colorless liquid	yellow liquid	red solid
yield	10.35 g (40.99 mmol, 88%)	9.68 g (38.33 mmol, 83%)	14.34 g (55.46 mmol, 67%)	6.48 g (23.77 mmol, 58%)	12.52 g (41.38 mmol, 90%)
NMR solv.	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
^{1}H NMR	6.80 (m, 2 H, ArH), 6.71 (m, 2 H, ArH), 3.06 (s, 2 H, HN), 0.21 (s, 18 H, $SiMe_3$)	6.50 (m, 4 H, ArH), 3.05 (s, 2 H, HN), 0.22 (s, 18 H, $SiMe_3$)	2.15 (d, 2 H, $^3J = 7.0$ Hz), 1.81 (m, 2 H), 1.57 (m, 2 H), 1.19 (m, 2 H), 1.03 (m, 2 H), 0.67 (s, 2 H, HN), 0.00 (s, 18 H, $SiMe_3$)	7.08 (m, 1 H, ArH), 7.02 (m, 1 H, ArH), 6.77 (m, 1 H, ArH), 6.65 (m, 1 H, ArH), 5.20 (s, 1 H, HN), 3.84 (d, 2 H, $^3J = 6.0$ Hz, CH_2), 0.30 (s, 9 H, $SiMe_3$), 0.12 (s, 9 H, $SiMe_3$)	7.21 (m, 2 H, ArH), 7.14 (m, 2 H, ArH), 6.65 (m, 2 H, ArH), 5.49 (s, 2 H, HN), 0.23 (s, 18 H, $SiMe_3$)
^{13}C NMR	137.6 (ArC), 120.2 (ArCH), 119.7 (ArCH), 0.4 ($SiMe_3$)	138.3 (ArC), 117.1 (ArCH), 0.0 ($SiMe_3$)	58.8 (ring C), 36.7 (ring CH_2), 25.5 (ring CH_2), 0.9 ($SiMe_3$)	147.3 (ArC), 129.5 (ArCH), 128.1 (ArCH), 128.1 (ArC), 117.1 (ArCH), 115.9 (ArCH), 45.5 (CH_2), 0.4 ($SiMe_3$), −0.4 ($SiMe_3$)	144.4 (ArC), 137.4 (ArC), 125.7 (ArCH), 121.3 (ArC), 120.4 (ArCH), 115.4 (ArCH), 0.1 ($SiMe_3$)
^{29}Si NMR	3.8	2.0	1.6	1.6, 5.5	3.6

O-(trimethylsilyl)carbamatobenzene (1 a)

Using the small autoclave, aminosilane **1** (0.80 g, 4.84 mmol) was dissolved in dry THF (2 mL) and exposed to 4 bar of CO_2 for 24 hours without stirring. After transferring the pale yellow liquid to a Schlenk flask and removing the solvent under reduced pressure, a white solid was obtained. Yield: 0.82 g (3.92 mmol, 81%). Recrystallization from *n*-pentane afforded colorless needles suitable for single-crystal X-ray analysis. Data of crystal structure determination are contained in the Supporting Information. ^{1}H NMR (400 MHz, THF-d8): δ 7.46–6.92 (m, 5H, ArH), 6.58 (s, 1H, NH), 0.30 (s, 9H, $SiMe_3$). ^{13}C NMR (101 MHz, THF-d8): δ 153.0 (CO), 140.8 (ArC), 129.4 (ArCH), 123.1 (ArCH), 118.9 (ArCH), 0.1 ($SiMe_3$). ^{29}Si NMR (79 MHz, THF-d8): δ 22.2.

For a large-scale reaction in the bigger autoclave, a solution of **1** (7.56 g, 45.73 mmol) in dry THF (20 mL) was exposed to 8 bar of CO_2 for 24 h. Following the described procedure led to a pale-yellow solid, which was dried under reduced pressure for 3 h. Yield: 8.62 g (41.18 mmol, 90%).

EA: calculated N 6.69%, C 57.38%, H 7.22%; found N 6.79%, C 57.14%, H 7.053%.

Calorimetric measurements

Calorimetric measurements using the aminosilane **1** were performed on a Setaram C80 instrument with a 9.5 cm^3 stainless steel vessel. Measurements were conducted isothermal at 30 °C in a pressure range from vacuum to 5 bar. Prior to measurements the vessel was evacuated for several hours. A sample of 50 to 100 mg pure aminosilane was inserted into the vessel in an argon atmosphere under ambient conditions. Carbon dioxide (from Linde, purity of 5.3) was provided by a pressurised tank. Regulation of the gas exposition was ensured by a stopcock separating the vessel and the gas tank. After inserting the deflated vessel into the instrument, equilibration of the setup was obtained before starting the measurement and loading the vessel with CO_2. The time period of the measurement varied between 18 to 21 hours. Evaluation of the experimental data gave an average enthalpy value of −76.7 +/− 5.2 kJ/mol for the insertion reaction at a pressure of 4 bar CO_2 using 54 mg (0.33 mmol) and 99 mg (0.60 mmol) aminosilane, respectively.

ω-[*O*-(trimethylsilyl)carbamato]toluene (2 a)

The aminosilane **2** (2.69 g, 15.00 mmol) was dissolved in dry THF (50 mL). CO_2 insertion reaction was performed by gas bubbling twice for 15 minutes at room temperature. The gas was dried prior to use by gas bubbling through pure sulfuric acid. After separating the solvent, the product was obtained as a white solid. Yield: 2.50 g (11.19 mmol, 75%).[7] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.31 (m, 5H, ArH), 5.62 (s, 1H, NH), 3.89–3.78 (m, 2H, CH_2), 0.37 (s, 9H, $SiMe_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8 (CO), 155.3 (CO), 143.1 (ArC), 138.8 (ArCH), 128.6–128.5 (ArCH), 127.5–126.8 (ArCH), 45.1 (CH_2), −0.03 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 23.6, 22.6.

Insertion reaction using the big autoclave afforded the pure product in higher yields. A solution of the aminosilane **2** (6.78 g, 37.83 mmol) in THF (20 mL) was charged with 8 bar CO_2 for 1 hour. By removal of the solvent **2 a** (7.90 g, 35.35 mmol, 93%) was gained as a white solid. NMR data confirmed the identity and purity of the product.

EA: calculated N 6.27%, C 59.16%, H 7.67%; found N 6.81%, C 59.02%, H 7.408%.

4-[*O*-(trimethylsilyl)carbamato]methoxybenzene (3 a)

A mixture of **3** (6.50 g, 33.28 mmol) and DBU (0.1 mL) in dry THF (20 mL) was exposed to 8 bar of CO_2 for 24 hours without stirring. After transferring the orange liquid to a Schlenk flask and removing the solvent under reduced pressure, a brownish solid was obtained (7.23 g, 30.21 mmol, 91%). Recrystallization from mother liquor afforded pale brown, needle-shaped crystals, which were used for unit cell determination by X-ray diffraction. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 1H, **3 a**, NH), 7.28 (d, $^3J = 8.9$ Hz, 2H, **3 a**, ArH), 6.71

(d, $^3J = 9.0$ Hz, 2H, **3a**, ArH), 6.59 (d, $^3J = 8.9$ Hz, 2H, **3**, ArH), 6.48 (d, $^3J = 8.9$ Hz, 2H, **3**, ArH), 3.59 (s, 1H, **3**, NH), 0.23 (s, 9H, $SiMe_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8 (CO), 153.0 (ArC–O), 141.3 (**3**, ArC–N), 132.6 (ArC–N), 120.3 (ArCH), 117.2 (ArCH), 116.2 (ArCH), 114.9 (ArCH), 114.2 (ArCH), 55.3 (OMe), 0.0 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 22.6 (O–$SiMe_3$), 7.3 ($Me_3SiOSiMe_3$), 1.7 (**3**, NH-$SiMe_3$).

1,2-bis[*O*-(trimethylsilyl)carbamato]benzene (4a)

The aminosilane **4** (0.51 g, 2.02 mmol) was dissolved in dry THF (2 mL) and exposed to 6 bar of CO_2 for 24 hours at room temperature without stirring. Eliminating the solvent under reduced pressure afforded a highly viscous liquid with a yellow-brownish color. Yield: 0.60 g (1.76 mmol, 87%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–6.58 (m, 4H, ArH), 3.32 (m, 2H, NH), 0.25 (s, 18H, $SiMe_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.3 (CO), 126.1 (ArC), 124.6 (ArCH), 120.0 (ArCH), 0.2 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 24.5.

1,4-bis[*O*-(trimethylsilyl)carbamato]benzene (5a)

A solution of **5** (9.68 g, 38.33 mmol) in dry THF (20 mL) was exposed to 8 bar of CO_2 for 24 hours at room temperature without stirring. The formation of a yellow precipitate inside a brownish liquid was observed during opening of the autoclave. The reaction mixture along with the precipitate was transferred into a Schlenk flask with the aid of 3×10 mL of dry THF. Removal of the solvent under reduced pressure afforded a yellow solid, which was dried in a dynamic vacuum for 2 hours. Yield: 12.26 g (36.00 mmol, 94%). ^1H NMR (400 MHz, $CDCl_3$): δ 6.57 (m, 4H, ArH), 3.35 (m, 2H, NH), 0.34 (s, 18H, $SiMe_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.2 (CO), 138.7 (ArC), 119.4 (ArCH), 116.8 (ArCH), 0.0 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 24.5, 23.9.

EA: calculated N 8.23%, C 49.38%, H 7.10%; found N 8.96%, C 50.30%, H 7.09%.

(+/−)-trans-1,2-bis[*O*-(trimethylsilyl)carbamato]cyclohexane (6a)

Exposing a solution of **6** (0.98 g, 3.79 mmol) in dry THF (2 mL) to 6 bar of CO_2 to for 24 h at room temperature without stirring afforded a white solid (after removal of the solvent under reduced pressure). Yield: 0.90 g (2.60 mmol, 67%). ^1H NMR (400 MHz, $CDCl_3$): numerous peaks. ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.7 (CO), 55.5 (ring CH), 32.6 (ring CH_2), 24.8 (ring CH_2), 0.1 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 22.7.

2-trimethylsilylamino-ω-[*O*-(trimethylsilyl)carbamato]toluene (7a)

A solution of aminosilane **7** (0.55 g, 2.02 mmol) in dry THF (2 mL) was exposed to 6 bar of CO_2 for 24 hours at room temperature without stirring. Afterwards, removal of the solvent under reduced pressure afforded a highly viscous, yellow liquid. Yield: 0.57 g (1.80 mmol, 89%).

Storage in the refrigerator gave needle-shaped crystals after several days. Analysis of the crystals by single-crystal X-ray diffraction revealed the crystal structure of the target compound. Data is collected in Table 7.

^1H NMR (400 MHz, $CDCl_3$): δ 7.07 (dt, 1H, $^3J = 7.7$ Hz, ArH), 6.96 (dd, 1H, $^3J = 7.4$ Hz, ArH), 6.76 (dd, 1H, $^3J = 8.0$ Hz, ArH), 6.58 (dt, 1H, $^3J = 7.3$ Hz, ArH), 5.48 (s, 1H, NH), 4.65 (s, 1H, NH), 4.18 (m, 2H, CH_2), 0.33 (s, 9H, $SiMe_3$), 0.26 (s, 9H, $SiMe_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.8 (CO), 155.7 (CO), 146.4 (ArC), 130.7 (ArCH), 129.0 (ArCH), 124.3 (ArCH), 116.8 (ArCH), 115.4 (ArCH), 43.0 (CH_2), −0.0 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 23.3 (O–$SiMe_3$), 2.8 (N–$SiMe_3$).

1,8-bis(trimethylsilylamino)naphthalene (8)

No reaction observed during exposure to 8 bar CO_2 for 24 hours.

A mixture of **8** (2 mL) in dry THF (10 mL) was exposed to 8 bar CO_2 pressure for 72 h. After transferring the deep red liquid to a Schlenk flask an NMR sample of the crude solution was analyzed. ^1H NMR (400 MHz, $CDCl_3$): numerous peaks. ^{13}C NMR (101 MHz, $CDCl_3$): numerous peaks. ^{29}Si NMR (79 MHz, $CDCl_3$): δ 24.9 (**8b**, O–Si), 23.8 (**8a**, O–Si), 23.6 (**8b**, O–Si), 22.8 (**8a**, O–Si), 13.8 (**8b**, N–Si), 13.0 (**8b**, N–Si), 7.2 (HMDSO), 3.3 (**8**), 1.2 (**8**).

Removal of solvent under reduced pressure for reducing the volume of the solution to ca. 50% and additional storage in the refrigerator led to the formation of white crystal blocks, which appeared red due to adherent mother liquor (*). Single-crystal X-ray structure determination revealed the structure of 1H-perimidin-2(3H)-one.

^1H NMR (400 MHz, $CDCl_3$): δ 9.45 (s, 2H, NH), 7.16–7.00 (m, 4H, ArH), 6.45 (dd, 2H, $^3J = 7.3$ Hz, ArH), 5.05 (s, 1H, NH, **8**), 3.59 (THF), 1.73 (THF), 0.12 (s, **8**), 0.01 (TMS). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.5 (CO), 147.0 (*), 138.9 (ArC–N), 135.8 (ArC), 128.6 (ArCH), 126.6 (*), 118.9 (ArCH), 115.2 (ArC), 111.2 (*), 104.8 (ArCH), 67.4 (THF), 25.2 (THF).

EA of 1H-perimidin-2(3H)-one: calculated N 15.21%, C 71.73%, H 4.38%; found N 15.39%, C 72.19%, H 4.538%.

Thermal decomposition of 1a

1a (1.12 g, 5.35 mmol, white solid) was placed in a small Schlenk flask and attached to a short-path distillation apparatus under inert conditions. The thermolysis experiment was performed under reduced pressure with constant stirring and heating in a silicone oil bath to a temperature of approximately 190 °C. A safety flask cooled with liquid nitrogen was installed between the still and the Schlenk line. The formation of a white solid in the neck of the flask, joint of the still and along the water-cooled cold finger was observed after 10 minutes. The temperature at the thermometer in the head of the still remained at 25 °C. The heating was stopped, parts of the white solid were removed for NMR analysis and the heating was resumed afterwards. Shortly after, the collection of a colorless liquid at the cold finger was observed. 20 minutes after beginning of heating the solid starting material was fully molten and white crystals formed in the joint between Schlenk flask and still. After 30 minutes the heating was stopped and the device was allowed to attain room temperature. Afterwards, NMR samples were taken from the cold finger, the safety flask and the residue. Analysis results are summarized in Table 3.

N,O-bis(trimethylsilyl)carbamatobenzene (1b)

The *O*-silylated carbamate **1a** (6.87 g, 32.82 mmol) was dissolved in dry *n*-pentane (100 mL) and mixed with Et_3N (3.40 g, 33.64 mmol) under constant stirring. While cooling with an ice bath, trimethylsilyltriflate (7.28 g, 32.73 mmol) was added dropwise, forming a cloudy precipitate, which settles on the bottom of the flask when stirring is interrupted. After 45 minutes of stirring under ice cooling the stirring was continued for another 2 hours at room temperature. Afterwards, the precipitate was frozen in a mixture of dry ice

Table 3. NMR analysis data of the thermal decomposition of **1 a**.

	1 a	10 min	residue	cold finger	safety flask
NMR solv.	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
^{1}H NMR	7.38–7.05 (m, 5H, ArH), 6.65 (s, 1H, NH), 0.34 (s, 9H, $SiMe_3$).	numerous peaks	numerous peaks	numerous peaks	numerous peaks
^{13}C NMR	153.0 (CO), 140.8 (ArC), 129.4 (ArCH), 123.1 (ArCH), 118.9 (ArCH), 0.1 ($SiMe_3$).	146.4 (**1 a**), 138.1 (**1 a**), 129.3 (**1 a**), 129.0 (**1 a**), 123.4 (**1 a**), 118.6 (**1 a**), 115.1 (**1 a**), 1.9 (HMDSO), 0.0 (**1 a**, TMS).	157.2, 152.2, 141.5, 138.2, 129.1, 128.7, 126.5, 123.4, 118.6, 116.0, 115.2, 2.0, 0.0	146.4, 138.1, 129.3, 129.0, 123.4, 120.7, 118.5, 117.4, 116.0, 115.1, 1.9, 0.0	146.4, 138.2, 129.3, 129.0, 123.4, 118.5, 115.1, 68.0 (THF), 25.6 (THF), 1.9 (HMDSO), 0.0 (TMS).
^{29}Si NMR	22.2	Inept: 24.7 (**1 a**), 7.3 (HMDSO), 0.0 (TMS)	24.5 (**1 a**), 23.5, 10.7, 7.4 (HMDSO), 2.8, 0.0 (TMS)	24.6 (**1 a**), 7.4 (HMDSO), 0.0 (TMS)	24.6 (**1 a**), 7.4 (HMDSO), 0.0 (TMS)

and isopropanol, and the liquid supernatant was separated by decantation. The precipitate fraction was washed with 20 ml of *n*-pentane. From the combined supernatant and washing, the solvent was removed under reduced pressure to yield a white solid, which was dried in a dynamic vacuum for a period of 2 hours to afford 7.69 g (27.32 mmol, 83 %) of **1 b**. Recrystallization from dry THF gave crystals suitable for single-crystal X-ray structure determination, which revealed the crystal structure of **1 b**. Data is collected in Table 7.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11–6.86 (m, 5H, ArH), 0.17 (s, 9H, $SiMe_3$), 0.00 (s, 9H, $SiMe_3$). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.0 (CO), 141.4 (ArC), 128.7 (ArCH), 128.5 (ArCH), 126.3 (ArCH), 0.5 ($SiMe_3$), −0.2 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 23.4 (O–$SiMe_3$), 10.7 (N–$SiMe_3$).

EA: calculated N 4.98 %, C 55.47 %, H 8.24 %; found N 5.07 %, C 55.01 %, H 8.215 %.

Thermal decomposition of 1 b

A sample of **1 b** (approx. 1 g) was transferred into the bottom ball of the three-parted Kugelrohr (ball tube) and connected to the Kugelrohr distillation device under inert conditions. The bottom ball (residue) and the intermediate fraction were placed inside the glass oven, while the outer bulb was cooled by water. The thermolysis experiment was performed under ambient pressure and with constant rotation of 20 rpm. The oven was heated to 170 °C, to 200 °C and to 230 °C for 30 minutes, respectively. At a temperature of approx. 100 °C melting of the white solid commenced and was completed at around 140 °C, thus forming a pale yellow liquid. At 200 °C, condensation of a colorless liquid in the middle bulb was observed. Up to a temperature of 230 °C colorless liquid reached the outer bulb as well, while the residue turned an intensive yellow. After cool down to room temperature the fractions were transferred into Schlenk flasks and samples for NMR spectroscopic measurements were taken. Due to the numerous peaks in the ^{13}C NMR spectra of the residue and the intermediate fraction, only the associated ^{29}Si NMR data are listed in Table 4.

ω-[*N,O*-bis(trimethylsilyl)carbamato]toluene (2 b)

A solution of the *O*-silylated carbamate **2 a** (30.33 g, 135.80 mmol) in dry diethylether (100 mL) was mixed with Et_3N (14.48 g, 143.07 mmol) under constant stirring and cooling with an ice bath. Trimethylsilyltriflate (32.62 g, 146.76 mmol) was added dropwise, leading to the formation of a cloudy precipitate, which settles on the bottom of the flask when the stirring is interrupted. The stirring was continued at room temperature until the next day. Afterwards, the precipitate was frozen in a mixture of dry ice and isopropanol, and the liquid supernatant was separated by decantation. The solvent was removed from the supernatant under reduced pressure to yield **2 b** (37.58 g, 127.17 mmol, 94 %) as a yellow, viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (m, 5H, ArH), 4.41 (s, 2H, CH_2), 0.33 (s, 9H, $SiMe_3$), 0.19 (s, 9H, $SiMe_3$), 0.09 (s, 18H, HMDSO). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.2 (CO), 140.4 (ArC), 128.4 (ArCH), 126.6 (ArCH), 126.4 (ArCH), 48.1 (CH_2), 2.0 (HMDSO), 0.8 ($SiMe_3$), 0.0 ($SiMe_3$). ^{29}Si NMR (79 MHz, $CDCl_3$): δ 22.6 (O–$SiMe_3$), 10.9 (N–$SiMe_3$), 7.1 (HMDSO).

Thermal decomposition of 2 b

A sample of **2 b** (3.13 g, 10.60 mmol) was placed in the bottom ball of the three-parted Kugelrohr (ball tube) and connected to the Kugelrohr distillation device under inert conditions. The bottom ball (residue) and the intermediate fraction were stored inside the

Table 4. NMR analysis data of the thermal decomposition of **1 b**.

	1 b	residue	intermediate fraction	outer fraction
NMR solv.	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
^{13}C NMR	157.0 (CO), 141.4 (ArC), 128.7 (ArCH), 128.5 (ArCH), 126.3 (ArCH), 0.5 ($SiMe_3$), −0.2 ($SiMe_3$).	numerous peaks	numerous peaks	134.0 (ArC), 129.7 (ArCH), 125.8 (ArCH), 124.9 (ArCH), 120.7 (NCO), 2.0 (HMDSO)
^{29}Si NMR	23.4 (O–$SiMe_3$), 10.7 (N–$SiMe_3$)	10.8, 8.6, 7.4 (HMDSO), 4.5	23.4 (**1 b**), 14.0, 12.5, 10.7 (**1 b**), 10.1, 7.3 (HMDSO), 4.5	7.1 (HMDSO)

Table 5. NMR analysis data of the thermal decomposition of **2b** in a three-parted Kugelrohr with stepwise heating.

	2b	residue	intermediate fraction	outer fraction
NMR solv.	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
^{13}C NMR	158.2 (CO), 140.4 (ArC), 128.4 (ArCH), 126.6 (ArCH), 126.4 (ArCH), 48.1 (CH_2), 0.8 ($SiMe_3$), 0.0 ($SiMe_3$).	numerous peaks	numerous peaks	144.1, 137.0 (ArC), 128.7 (ArCH), 127.8 (ArCH), 126.6 (ArCH), 120.7 (NCO), 46.4 (CH_2), 1.7 (HMDSO)
^{29}Si NMR	22.6 (O–$SiMe_3$), 10.9 (N–$SiMe_3$)	22.3, 15.9, 7.4 (HMDSO), −21.8	29.6, 27.5, 22.7 (**2b**), 19.2, 11.0 (**2b**), 9.8, 7.1 (HMDSO), 3.3, 2.2	7.3 (HMDSO)

glass oven and the outer bulb was cooled by water. The thermolysis experiment was performed under ambient pressure and with constant rotation of 20 rpm. For a period of 45 minutes, the apparatus was tilted at a 45-degree angle to allow some reflux. The oven was heated to 200 °C, to 250 °C and to 300 °C for 30 minutes, each. Beginning at a temperature of approx. 250 °C the collection of a clear, colorless liquid in the outer bulb was observed. With the increased temperature of 300 °C the residue progressively adopted a dark brown color and increased in viscosity. After cool down to room temperature the fractions were transferred into Schlenk flasks and samples for NMR spectroscopic measurements were taken. Due to the numerous peaks in the ^{13}C NMR spectra of the residue and the intermediate fraction, only the associated ^{29}Si NMR data are listed in Table 5. The overall intensity of the signals in the ^{29}Si NMR spectrum of the residue is very low resulting in a bad signal-to-noise ratio.

Table 6. NMR analysis data of the thermal decomposition of **2b** in a three-parted Kugelrohr with direct heating to 300 °C.

	2b	residue	intermediate fraction	outer fraction
NMR solv.	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$
^{13}C NMR	158.2 (CO), 140.4 (ArC), 128.4 (ArCH), 126.6 (ArCH), 126.4 (ArCH), 48.1 (CH_2), 0.8 ($SiMe_3$), 0.0 ($SiMe_3$).	numerous peaks	numerous peaks	137.9 (toluene, ArC), 129.2 (toluene, ArCH), 128.4 (toluene, ArCH), 125.5 (toluene, ArCH), 21.5 (toluene, CH3), 2.0 (HMDSO), 0.8 (Me_3SiNCO)
^{29}Si NMR	22.6 (O–$SiMe_3$), 10.9 (N–$SiMe_3$)	16.9, 7.4 (HMDSO), 4.4, −21.8	7.4 (HMDSO), −21.9	7.3 (HMDSO), 4.2 (Me_3SiNCO)

Table 7. Crystallographic and structure refinement data for compounds **1b** and **7a**.

	N,O-bis(trimethylsilyl) carbamatobenzene (**1b**)	2-trimethylsilylamino-ω-[*O* (trimethylsilyl)carbamato] toluene (**7a**)
empirical formula	$C_{13}H_{23}NO_2Si_2$	$C_{14}H_{26}N_2O_2Si_2$
formula weight	281.50	310.55
temperature [K]	160(2)	180(2)
crystal system	Monoclinic	Triclinic
space group	$P2_1/c$	P-1
a [Å]	13.1210(7)	10.9652(4)
b [Å]	7.3166(2)	14.3342(5)
c [Å]	17.6436(10)	18.7251(6)
α [°]	90	92.844(3)
β [°]	90.266(5)	101.678(3)
γ [°]	90	101.501(3)
volume [$Å^3$]	1693.79(14)	2811.93(17)
Z	4	6
ρ_{calc} [mg/cm^3]	1.104	1.100
absorption coefficient [mm^{-1}]	0.205	0.192
F(000)	608	1008
reflections collected/unique	29493/3694 [R(int) = 0.0313]	27102/9887 [R(int) = 0.0414]
data/restraints/parameters	3694/0/169	9887/7/600
goodness-of-fit on F^2	1.057	1.046
Final R indices [I > 2sigma(I)]	R1 = 0.0364, wR2 = 0.0916	R1 = 0.0483, wR2 = 0.1125
R indices (all data)	R1 = 0.0491, wR2 = 0.1000	R1 = 0.0759, wR2 = 0.1238
extinction coefficient	n/a	0.0038(6)
largest diff. peak and hole [$e \cdot Å^{-3}$]	0.277 and −0.305	0.534 and −0.345

Table 8. Data of unit cell determination and structure refinement for compounds **1a**, perimidone, two modifications of *N*-(trimethylsilyl) carbamatocyclohexane and di(*N*-phenylcarbamoyloxy)dimethylsilane.

	N-(trimethylsilyl) carbamato-benzene (**1a**)	perimidone	*N*-(trimethylsilyl) carbamato-cyclohexane	N-(trimethylsilyl) carbamato-cyclohexane	di(*N*-phenyl carbamoyloxy) dimethylsilane
empirical formula	$C_{10}H_{15}NO_2Si$	$C_{11}H_8N_2O$	$C_{10}H_{21}NO_2Si$	$C_{10}H_{21}NO_2Si$	$C_{16}H_{18}N_2O_4Si$
formula weight	209.32	184.19	215.37	215.37	330.41
temperature [K]	200(2)	180(2)	145(2)	180(2)	150(2)
crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	Pbca	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pca2_1$
a [Å]	9.5592(4)	14.0569(16)	11.1378(6)	11.0607(6)	27.9900(19)
b [Å]	19.3737(11)	4.5923(3)	12.3898(5)	12.4051(9)	5.1720(3)
c [Å]	12.2437(6)	13.1708(16)	9.4183(5)	9.7141(5)	11.0443(11)
β [°]	90	99.505(9)	97.513(4)	100.490(4)	90
volume [$Å^3$]	2267.50(19)	838.55(15)	1288.52(11)	1310.59(14)	1598.8(2)
Z	8	4	4	4	4
ρ_{calc} [mg/cm^3]	1.226	1.459	1.110	1.091	1.373
absorption coefficient [mm^{-1}]	0.183	0.097	0.162	0.160	0.169
F(000)	896	384	472	472	696
reflections collected/unique	15031/2219 [R(int) = 0.0405]	12857/1824 [R(int) = 0.0466]	20134/3113 [R(int) = 0.0480]	13105/3159 [R(int) = 0.0279]	16379/3711 [R(int) = 0.0470]
data/restraints/parameters	2219/0/134	1824/0/135	3113/0/134	3159/7/201	3711/1/218
goodness-of-fit on F^2	1.064	1.042	1.084	1.044	1.054
final R indices [I > 2sigma(I)]	R1 = 0.0347, wR2 = 0.0810	R1 = 0.0370, wR2 = 0.0918	R1 = 0.0375, wR2 = 0.0884	R1 = 0.0400, wR2 = 0.1041	R1 = 0.0398, wR2 = 0.0960
R indices (all data)	R1 = 0.0516, wR2 = 0.0908	R1 = 0.0558, wR2 = 0.1006	R1 = 0.0490, wR2 = 0.0953	R1 = 0.0503, wR2 = 0.1114	R1 = 0.0580, wR2 = 0.1052
largest diff. peak and hole [$e·Å^{-3}$]	0.210 and −0.274	0.226 and −0.184	0.304 and −0.248	0.263 and −0.262	0.375 and −0.311

Direct heating of **2b** (8.38 g, 28.36 mmol) to 300 °C in a three-parted Kugelrohr for 2.5 hours resulted in the formation of toluene instead of the desired benzyl isocyanate. The experiment was carried out under reflux for 1 hour by tilting the apparatus to a 45-degree angle before moving back to a horizontal orientation for another 1.5 hours. While the residue turned brown and highly viscous, a colorless liquid with a white precipitate accumulated inside the outer bulb. After cool down to room temperature the fractions were transferred into Schlenk flasks using $CDCl_3$ for washing. NMR spectroscopic measurements were performed afterwards. Due to the numerous peaks in the ^{13}C NMR spectra of the residue and the intermediate fraction, only the associated ^{29}Si NMR data are listed in Table 6. The overall intensity of the signals in the ^{29}Si NMR spectrum of the residue is very low resulting in a bad signal-to-noise ratio.

Crystal structure data

Table 7 and Table 8 contain crystal structure data for all compounds, which are mentioned in this manuscript and were analyzed by X-ray diffraction analysis.

Deposition Numbers 2060544 (for **1a**), 2060545 (for di(*N*-phenylcarbamoyloxy)dimethylsilane), 2060546 (for perimidone), 2060547 (for **1b**), 2060548 (for **7a**), 2060549 (for N-(trimethylsilyl) carbamatocyclohexane at 180 K), and 2060550 (for N-(trimethylsilyl) carbamatocyclohexane at 145 K) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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